



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C02F 11/14, 1/56	A1	(11) International Publication Number: WO 99/50195 (43) International Publication Date: 7 October 1999 (07.10.99)
(21) International Application Number: PCT/GB99/00991 (22) International Filing Date: 30 March 1999 (30.03.99) (30) Priority Data: 9807047.7 1 April 1998 (01.04.98) GB (71) Applicant (for all designated States except US): CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED [GB/GB]; Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): ALLEN, Anthony, Peter [GB/GB]; 6 Ivy Grove, Shipley, West Yorkshire BD18 4JZ (GB). (74) Common Representative: CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED; Patents Dept., Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DEWATERING OF ORGANIC SUSPENSIONS WITH ANIONIC AND CATIONIC POLYMERS		
(57) Abstract <p>A process of dewatering an aqueous suspension of suspended organic solids comprising adding to the suspension an aqueous composition comprising a first water-soluble ionic polymeric flocculant and a second water-soluble ionic polymeric flocculant in which the first flocculant is in excess over the second flocculant and the first and second flocculants are counterionic and in the aqueous composition at least a portion of the first flocculant and at least a portion of the second flocculant form particles of counterionic precipitate. Characterised in that the particles of counterionic precipitate are of size at least 90 wt.% above 100 nm in the aqueous composition and substantially all of the portion of the first flocculant which is not contained in the particles of counterionic precipitate is in solution.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

DEWATERING OF ORGANIC SUSPENSIONS WITH ANIONIC AND CATIONIC POLYMERS

This invention relates to processes for dewatering suspensions containing organic material and to novel products which can be used in such processes.

It is well known to dewater aqueous suspensions containing suspended solid organic material (organic suspensions), such as sewage sludge, waste waters, textile industry effluents etc, by mixing into the suspension polymeric flocculant, allowing the suspended particles to flocculate and dewatering the flocculated suspension.

High molecular weight cationic polymeric flocculants are commonly used for this purpose. It is also known to use two different polymeric flocculants in the same process and in commercial practice these are usually both cationic.

There are some suggestions in the published prior art to carry out the flocculation and dewatering of organic suspensions by using a cationic polymeric flocculant and an anionic polymeric flocculant.

It is well known that many combinations of counterionic flocculants, when mixed in solution, will tend to form a precipitate due to counterionic precipitation. Therefore if counterionic flocculants are used they are often added to the suspension sequentially rather than simultaneously. Our International Publication WO92/00248 addresses this problem in an alternative way. We describe a process of providing anionic and cationic flocculants as solid particles which are mixed directly into the suspension. This can require prolonged mixing of the flocculants into the suspension in order to ensure that they dissolve.

It is known to provide blends of anionic and cationic polymers but under conditions which prevent counterionic precipitation occurring. It can be prevented with the use of added acid or inorganic salt or by careful choice of polymer type.

Examples of various systems in which both anionic and cationic flocculants are used include JP 07/100,500, JP 61/200,897, Kulicke et al, Chem.-Ing.-Tech.(1993), 65(5), 541-52, JP 05/038,404, JP 04/300,700, JP 02/009,500, JP 62/289,300, JP 62/129,200, JP 61/234,999, JP 58/215,454, JP 58/216,706 and JP 58/060,094. US 3,539,510 specifies the choice of monomer type for the cationic polymer in order to prevent counterionic precipitation and JP 63/252,600 provides a blend as an emulsion.

This does not affect the general situation that aqueous solution blends of cationic and anionic polymers are generally avoided because of the counterionic precipitation problem.

In our International Publication WO97/06111 we describe an invention based on the discovery that in the pressure dewatering of mineral suspensions having mineral solids content of at least 150 g/l use of a blend of anionic and cationic flocculants in which anionic flocculant is in excess and in which counterionic precipitation does occur can be beneficial for these particular systems.

In our publication EP-B-202,780 we describe the use of polymeric material for the flocculation of suspended solids in which the polymeric material comprises polymeric particles. These particles have dry size of below 10 μm . In this publication we explain that if desired the particles can be produced by co-precipitation of anionic and cationic polymers and that an excess of water-soluble polymer of one ionic type can be used. Examples 9 and 10 describe the flocculation and dewatering of activated sewage sludge. Dewatering is carried out on a laboratory centrifuge. Flocculation is effected by a blend of a cationic copolymer of DMAEAMeCl and acrylamide and an anionic copolymer of sodium acrylate and acrylamide. The blend is formed by first producing a solution of anionic polymer and a separate solution of cationic polymer and then mixing the preformed solutions. This blend contains an excess of cationic polymer. Mixing of the preformed solutions is rapid. These examples state that when mixing is insufficiently rapid a precipitate settles. That blend is thus not used. Particles produced in the blends used in these examples will be of size below 10 μm , as required by the disclosure of this publication.

It would be desirable to provide an improved method of dewatering organic suspensions such as sewage sludge, in particular to provide increased cake solids after dewatering.

According to a first aspect of the invention we provide a process of dewatering an aqueous suspension of organic suspended solids (an organic suspension) comprising adding to the suspension an aqueous composition comprising a first water-soluble ionic polymeric flocculant and a second water-soluble ionic polymeric flocculant in which the first flocculant is in excess over the second flocculant and the first and second flocculants are counterionic and in the aqueous composition at least

a portion of the first flocculant and at least a portion of the second flocculant together form particles of counterionic precipitate, allowing the suspended solids to flocculate and dewatering the the flocculated suspension, characterised in that the particles of counterionic precipitate are of size at least 90 wt.% above 100 μm in the aqueous composition and substantially all of the portion of the first flocculant which is not contained in the particles of counterionic precipitate is in solution. We have found surprisingly that, contrary to the teaching in the prior art, good results can be obtained with the combined simultaneous use of counterionic flocculants for flocculating organic suspensions even when visible counterionic precipitate is obtained. This is contrary to normal commercial practice which is to use co-ionic cationic flocculants (in cases where two or more different flocculants are used). We also find that, also contrary to the general understanding in the art, use of an aqueous composition containing large particles of counterionic precipitate can give improved dewatering of organic suspensions.

We also find surprisingly that although systems of this general type are described in our publication WO97/06111, in which excess of anionic flocculant is used, and in which the suspension is a high solids mineral suspension, systems containing counterionic precipitate can be used in cases where cationic flocculant is in excess and can be used for treating organic suspensions.

When activating polymer with water (i.e. dissolving the polymer) prior to adding it to an organic suspension for flocculation, normal practice requires that the activated aqueous composition should be as homogeneous as possible and should contain substantially no visible evidence of precipitated or gelatinous material. In the invention, however, we find that improved performance is obtained even though the aqueous composition, on close examination, may be seen to be less homogeneous, often substantially less homogeneous, than would normally thought to be desirable, and contains visible particles of counterionic precipitate.

The organic suspension is a suspension of particulate material of which at least some is organic (rather than inorganic or mineral). It preferably contains, by weight of dry solids, at least 10 wt.% organic material, more preferably at least 30 wt.%. Generally it is wholly or mainly organic and has organic content at least 50 wt%, preferably at least 70 wt.%.

The process can be advantageous when the organic suspension has a content of inorganic suspended solids, for instance at least 10 or 20 wt% or even at least 30 wt%. Coarse organic solid particles, e.g. of size 90 wt% above 100 μ m or above 200 μ m, even above 500 μ m or 1mm, can be advantageous.

The solids content of the suspension can be low, e.g. 0.1% to 1.5% or 2% but preferably the suspension is a sludge having organic solids content at least 2% and up to 15% or 20% (measured as weight dry solids on volume of suspension), often from 1% or 3% to 10%, for instance 1 to 5 or 8%.

Suitable organic suspensions which can be treated using the process of the invention include sewage and sewage sludges; cellulosic sludges such as pulp and paper mill sludges and deinking sludges (which can have up to 50% inorganic solids content); animal processing and food processing sludges and textile industry effluents. The process can also be used for the treatment of sludges produced during the treatment of potable water.

In the process the organic suspension is treated with an aqueous composition which comprises a first water-soluble ionic polymeric flocculant and a second water-soluble ionic polymeric flocculant.

In the aqueous composition the first flocculant is in excess over the second flocculant. For instance the ratio by weight of the first:second flocculant may be at least 1.5:1, generally at least 2:1. Often it is from 15:1 to 2:1, preferably 12:1 to 4:1 by weight.

In the aqueous composition the first and second flocculants are counterionic. That is, one is a flocculant which is anionic and one is a flocculant which is cationic.

The anionic polymeric flocculant may be a water-soluble homopolymer of water-soluble ethylenically unsaturated anionic monomer, or it may be a water-soluble copolymer of a water-soluble ethylenically unsaturated anionic monomer blend. Generally at least 3 wt%, often at least 5, 10 or 15 wt% but generally not more than 50 or 60 wt% of the monomers are anionic with any other monomers being non-ionic.

The anionic polymer may be a polymer of a type often described as substantially non-ionic but containing a low amount of anionic monomer, for instance around 1 or 2 wt%. This anionic content may be present as a result of hydrolysis of non-ionic monomer such as acrylamide. In this specification we encompass such

polymers within the scope of "anionic polymers" provided they have high enough anionic content to give co-precipitation with the cationic flocculant which is used and form particles of counterionic precipitate as defined above.

Preferred anionic monomers are ethylenically unsaturated carboxylic or sulphonic acids, generally as their water-soluble alkali metal salts. Examples are 2-acrylamido-2-methyl propane sulphonic acid (AMPS, US trade mark), methacrylic acid and acrylic acid (as sodium or other alkali metal salt). Sodium acrylate is usually preferred.

Suitable water-soluble ethylenically unsaturated non-ionic comonomers include acrylamide and methacrylamide.

Preferred anionic flocculants are copolymers of acrylamide and, usually, 10 to 60% by weight sodium acrylate, in particular copolymers of 10 to 30 wt.% sodium acrylate and 70 to 90 wt.% acrylamide. Alternatives include homopolymers of sodium acrylate and copolymers of acrylamide and AMPS, in particular copolymers of AMPS and up to 97wt%, often up to 95wt%, (meth) acrylamide. A blend of polymers may be used.

The anionic flocculant should be water-soluble. It can be a high molecular weight bridging flocculant having intrinsic viscosity (IV) of at least about 5, preferably at least 8, often at least 10 dl/g. IV may be as high as 30dl/g or greater and is often in the range 10 to 20 dl/g. Alternatively it can be a low molecular weight coagulant material of IV below 3 or 4 dl/g. Generally IV is at least 1 dl/g.

In this specification intrinsic viscosity is measured by suspended level viscometer in buffered pH7 1M NaCl at 25°C.

The cationic polymeric flocculant may be a homopolymer or a copolymer of two or more monomer types. It may be a mixture of two or more polymers. The polymer may be a naturally occurring cationic polymer or a modified naturally occurring cationic polymer, but is preferably a synthetic polymer.

The cationic polymeric flocculant is usually formed from a water-soluble ethylenically unsaturated monomer or monomer blend. The polymer may be formed from monomers of which substantially 100% are water-soluble cationic ethylenically unsaturated monomers. It is preferably formed from a water-soluble blend of cationic and non-ionic ethylenically unsaturated monomers.

The amount of cationic monomer is usually 10 to 80%, often 10 to 60%, by weight with the remainder usually being acrylamide or other water-soluble ethylenically unsaturated monomer.

As with the anionic flocculant, the cationic flocculant may be a polymer having a rather low amount of cationic monomer such that it might be described as a substantially non-ionic polymer. For instance, it may contain around 1 or 2 wt.% cationic monomer. In this specification we encompass such polymers within the term "cationic flocculant", provided that they comprise sufficient cationic content to form a counterionic precipitate with the anionic flocculant, as defined above.

Suitable cationic monomers include dialkylaminoalkyl (meth)-acrylates and -acrylamides, as acid addition or, preferably, quaternary ammonium salts, and diallyl dialkyl ammonium halides. Preferred acrylates and (meth) acrylates are di-C₁₋₄ alkylaminoethyl (meth) acrylates and preferred acrylamides are di-C₁₋₄ alkylaminopropyl (meth) acrylamides, in particular dimethylaminoethyl (meth) acrylates (DMAE(M)A) and dimethylaminopropyl (meth) acrylamide (DMAP(M)A), with the respective methacrylate and methacrylamide compounds being particularly preferred, as acid addition and, preferably, quaternary ammonium salts. The preferred diallyl dialkyl ammonium halide is diallyl dimethyl ammonium chloride (DADMAC).

The preferred cationic polymers are copolymers of dialkylaminoalkyl-(meth)acrylate and -(meth)acrylamide monomers with acrylamide or other non-ionic monomer.

The cationic polymer is preferably a high molecular weight bridging flocculant, typically having intrinsic viscosity at least 4 dl/g and preferably at least 6 and typically up to 12 or even 17 dl/g or higher.

Both the anionic and cationic polymeric flocculants are essentially water-soluble, but either polymeric material may be of the type described in EP 202,780 containing a soluble fraction and a particulate insoluble fraction having a particle size below 10µm. If used, the soluble fraction of such a polymer will be such that it forms the particles of counterionic precipitate of the large size defined above.

An advantage of the invention is that the flocculants are not restricted by considerations of compatibility and thus it is not necessary to use, for instance, free

base cationic or free acid anionic flocculant in an attempt at minimising incompatibility, and it is not necessary to add acid, salt or other additives in order to minimise incompatibility. Instead, the flocculants can be the conventionally available flocculants mixed under conditions whereby counterionic precipitation can occur, that is to say some degree of non-homogeneity will be seen to exist if the defined amounts of the selected polymers are activated gently, without application of sufficient shear to disperse any counterionic precipitate which is formed.

In the aqueous composition used in the process of the invention the first polymeric flocculant which is in excess is preferably the cationic flocculant. In such compositions the cationic flocculant forms the defined particles of counterionic precipitate with the second, anionic flocculant. Because of the excess of cationic flocculant not all of the cationic flocculant will be incorporated into such particles. The remainder is substantially entirely in solution and is thus available for flocculating the organic suspension when the aqueous composition is mixed into the suspension. Little or none of the cationic flocculant (except that in the particles of counterionic precipitate) should remain in its initial undissolved powder or emulsion form. Instead it should substantially all have gone into solution, with the exception of the proportion which has been incorporated into the particles of counterionic precipitate. Preferably at least 50 wt.%, more preferably at least 75 wt.% of the total amount of cationic flocculant in the aqueous composition is in solution.

Organic suspensions which can be treated using compositions containing excess cationic flocculant include sewage sludges and waterworks sludges which result from the treatment of waters containing large amounts of organic substances such as humic acids or algae.

In other processes of the invention the first polymeric flocculant is the anionic flocculant which is in excess over the cationic flocculant.

We believe that in the formation of these aqueous compositions the anionic polymeric flocculant initially goes substantially wholly into solution but some of it is then precipitated onto or with the cationic flocculant to form a precipitate.

In these compositions the anionic flocculant should be substantially completely dissolved, in the sense that little or none of it should remain in its initial undissolved powder or emulsion form and instead it should substantially all have gone into

solution although some will have been incorporated into counterionic precipitate. In practice it is generally desirable that at least 50% by weight, and preferably at least 75% by weight of the amount of anionic flocculant which is introduced into the aqueous composition should be in solution.

It is generally preferred that in this case the process is conducted so that the anionic polymer forms a type of coacervate or precipitate around the cationic polymer.

Organic suspensions which can be treated using aqueous compositions containing excess anionic flocculant include suspensions produced during drinking water treatment. In drinking water treatment dissolved, colloidal and suspended substances naturally present in the water are coagulated by addition of ferric or aluminium salts and then the resulting flocs are removed by settlement or flotation and subsequently filtration. The sludge thus produced is composed of the substances present in the untreated water and hydrolysed metal coagulant salts. Some sludges produced from relatively clean waters or from waters containing significant amounts of inorganic substances such as clay particles may respond to treatment using compositions having excess anionic flocculant.

In the aqueous composition used in the process of the invention the anionic and cationic flocculants together form particles of counterionic precipitate. These are large, in that in the solution they are of size at least 90 wt.% above 100 μm , often at least 90 wt.% above 200 μm . They may be of size up to 1mm, for instance 90 wt.% between 300 and 800 μm . Usually the particles of counterionic precipitate are visible to the naked eye in the composition. This is in contrast with the system described in EP-B-202,780 in which any particles of counterionic precipitate must be of size below 10 μm .

The aqueous composition generally has a total polymer content (i.e. anionic + cationic) of 0.001 to 5% by weight, more usually around 0.01 to 1% by weight. Preferred polymer content ranges from 0.1 to 0.5%, for instance around 0.3%.

The aqueous composition may be produced in any manner which results in the presence of particles of counterionic precipitate having the defined size. Preferably the polymers are supplied initially as reverse phase emulsions (which may be anhydrous) or, more preferably, powders. Accordingly the aqueous composition is

generally formed by mixing into water the polymers in powder form or the polymers in emulsion form. Preferably the aqueous composition is formed by mixing into water the polymers in powder form.

The polymers may be mixed sequentially or simultaneously into the water which is to provide the aqueous composition but generally they are mixed simultaneously. Preferably they are provided as a preformed blend of the polymers, and this blend is mixed into water. Thus preferably the polymers are supplied as a blend of cationic polymer powder and anionic polymer powder and this blend is mixed with sufficient dilution water to form the aqueous composition having a polymer content of below 5% in which the excess first flocculant is dissolved.

The mixing of the polymers into water to form the aqueous composition may be performed in conventional make-up apparatus. After initial mixing and before addition to the suspension it is generally preferred to allow the dilute aqueous composition to age, optionally with mixing, to allow substantially all of the first flocculant polymer which is in excess to go into solution. This may require ageing for instance for at least 10 minutes, and often at least 30 minutes, and frequently at least an hour when either or both polymers is supplied as a powder. Mixing should be carried out in such a way that the particles of counterionic precipitate which are formed are not subsequently broken up or redispersed.

The polymers which are used in the invention can be made by conventional techniques. For instance, polymer powders may be made by bulk gel polymerisation followed by comminution and drying or by reverse phase bead polymerisation followed by drying and optionally comminution.

In the invention the term "dewatering" includes thickening, for instance to a final solids content of from 2 to 10%. Preferably it is dewatering to produce a cake which is as dry as possible, for instance dewatering under pressure.

In the invention the aqueous composition should be produced and dosed into the organic suspension in such a way that the counterionic precipitate of particle size as defined above is formed and retained until dosing takes place, so that the defined counterionic precipitate particles are present in the aqueous composition when it is added to the organic suspension.

We believe that the thorough mixing of the flocculant into the organic suspension is important, and if inferior results are obtained in a process it may be desirable to increase the shear applied during the mixing.

In particular we believe that an increase in shear at some point during the mixing and flocculation stages can be beneficial. This can be achieved in dewatering processes which produce a cake when shear is applied during the formation of the cake of flocculated solids or during the passage of the treated suspension to the cake formation stage. The increase in shear can be provided for instance by using a centrifuge to carry out the dewatering stage. During centrifugation the solids are conveyed along the bowl of the centrifuge by a rotating scroll.

Dosing of the aqueous flocculants into the suspension can be effected in a manner conventional for liquid flocculants. Normally it is adjusted so as to give substantially constant dosage of the flocculant polymers per unit volume of the suspension.

Dosage of polymer will generally depend on the type of dewatering process chosen. For centrifugation dewatering the amount of polymer is often 5 to 15 kg polymer per ton dry solids in the suspension, for instance 5 or 7 to 10 kg/tds. This can be used in processes in which anionic flocculant is in excess and in processes in which cationic flocculant is in excess. In belt pressing processes (which can be used for dewatering suspensions of the type treated with aqueous compositions containing excess cationic flocculant), the dosage of flocculant is often from 5 to 10 kg/tds. Filter pressing is often used for dewatering suspensions which have been treated with compositions having anionic excess. Polymer dosage can be for instance 2 to 5 kg/tds.

For the purposes of this invention, it can be assumed that the defined blends of excess of the first flocculant with a minor amount of the second flocculant are blends which will give counterionic precipitation unless compatibilising components are added to minimise this, and in the invention these are unnecessary.

Dewatering (including thickening) can be by any suitable means, and is preferably by pressure dewatering. Suitable methods include vacuum filtration, filter pressing and belt pressing. Dewatering by centrifuge is preferred.

When the dewatering process provides a cake, the percentage of solids in the cake should be as high as possible. Typical cake solids produced by centrifugation of sludges from drinking water treatment are from 15 to 25 wt.% and from filter pressing of similar suspensions are 20 to 40 wt.%. Improvements in cake solids of for instance at least 1, e.g. 2 to 4 percentage units, are considered beneficial.

In treatment of waterworks sludges or sewage sludges cake solids from centrifugation tend to be 20 to 30 wt.%, from belt pressing 18 to 28 wt.% and from filter pressing 25 to 35 wt.%. Again, an increase in cake solids of at least 1 percentage point, for instance from 2 to 4 percentage points, is considered beneficial.

A second aspect of the invention provides a composition which is particularly suitable for use in the process. This aspect of the invention provides an aqueous composition comprising 2 to 20 parts by weight of water-soluble cationic polymeric flocculant and one part by weight water-soluble anionic polymeric flocculant and sufficient water to give a polymer concentration of below 5% in which the anionic and cationic polymeric flocculants form stably suspended particles of counterionic precipitate of size at least 90 wt.% above 100 μm and substantially all the cationic polymer which is not part of the counterionic precipitate is in solution.

The particles can be formed as a coacervate of polymer of one ionic type around a core of the opposite ionic type. Any of the composition features described above may be applied to this aspect of the invention.

The following examples is an illustration of the invention.

Example 1Preparation of Polymer Blend A

A cationic powder grade copolymer of acrylamide and dimethylaminoethyl acrylate, methyl chloride quaternary ammonium salt of cationicity 56.9 weight % and intrinsic viscosity above 7 dl/g is mixed with an anionic powder grade copolymer of sodium acrylate with acrylamide of anionicity 10 weight % and intrinsic viscosity above 7 dl/g in a ratio cationic: anionic of 8:1. This blend is then mixed with sufficient water to form a 1% aqueous solution, wherein small globules of anionic polymer are suspended in the cationic polymer solution.

Example 2Preparation of Polymer Blend B

Example 1 is repeated except using an anionic powder grade copolymer of sodium acrylate with acrylamide of intrinsic viscosity above 7 dl/g and anionicity 13 weight % instead of 10 weight % in the ratio cationic : anionic of 10:1. The blend is dissolved in water as in example 1.

Example 3Preparation of polymer Blend C

Example 1 is repeated except using an anionic powder grade copolymer of sodium acrylate with acrylamide of intrinsic viscosity above 7 dl/g and anionicity 24 weight % instead of 10 weight % in the ratio cationic : anionic of 10:1. The blend is dissolved in water as in example 1.

Example 4Preparation of Polymer Blend D

Example 3 is repeated except using a cationic powder grade copolymer of dimethylaminoethyl acrylate, methyl chloride quaternary ammonium salt with acrylamide of intrinsic viscosity above 7 dl/g and cationicity 69.5 weight % instead of 56.9 weight % in the ratio cationic : anionic 10:1. The blend is dissolved in water as in example 1.

Example 5Use of Polymer Blends for dewatering Sewage Sludge

A 500ml sample of sewage sludge diluted with water (2:3) is mixed with polymer blend. The treated sludge was then subjected to high shear. The flocculated sludge is then transferred to a damp filter cloth through which the filtrate was allowed to drain. The volume of filtrate collected was measured after 5 seconds and after 10 seconds. The results are shown in table 1.

Table 1

Polymer Blend	Dose (mg cationic polymer per litre diluted sludge)	Volume of filtrate after 5 seconds (ml)	Volume of filtrate after 10 seconds (ml)
A	100	250	360
A	120	300	395
A	140	310	405
A	160	315	400
B	100	250	365
B	120	308	400
B	140	300	400
C	100	235	340
C	120	285	385
C	140	310	400
C	160	300	400
D	100	260	370
D	120	315	400
D	140	300	400

As can be seen from the results all of the anionic polymer blends show good dewatering characteristics, particularly after 10 seconds free drainage.

CLAIMS

1. A process of dewatering an aqueous suspension of suspended organic solids comprising

adding to the suspension an aqueous composition comprising a first water-soluble ionic polymeric flocculant and a second water-soluble ionic polymeric flocculant in which the first flocculant is in excess over the second flocculant and the first and second flocculants are counterionic and in the aqueous composition at least a portion of the first flocculant and at least a portion of the second flocculant form particles of counterionic precipitate

characterised in that the particles of counterionic precipitate are of size at least 90 wt.% above 100 μm in the aqueous composition and substantially all of the portion of the first flocculant which is not contained in the particles of counterionic precipitate is in solution.

2. A process according to claim 1 in which the proportion of organic material in the suspension is at least 30 wt.%, preferably at least 70 wt.%, by weight of dry solids.

3. A process according to claim 1 or claim 2 in which the solids content of the suspension is from 1 to 10 wt.% (weight dry solids by volume of suspension).

4. A process according to any preceding claim in which the ratio by weight of first:second flocculant is from 2:1 to 20:1.

5. A process according to any preceding claim in which the first flocculant is a cationic flocculant.

6. A process according to any preceding claim in which the aqueous composition comprises water-soluble cationic polymeric flocculant having intrinsic viscosity at least 4 dl/g and water-soluble anionic polymeric flocculant having intrinsic viscosity at least 5 dl/g.

7. A process according to any preceding claim in which the particles of counterionic precipitate are of size in the aqueous composition at least 90 wt.% from 300 to 800 μm .

8. A process according to any preceding claim in which the aqueous composition is made by mixing simultaneously into water powder anionic polymeric flocculant and powder cationic polymeric flocculant, preferably as a preformed powder blend.

9. A process according to claim 8 in which the powder polymer has been made by gel polymerisation and comminution or reverse phase bead polymerisation and optional comminution.
10. A process according to any preceding claim comprising dewatering the suspension under pressure, preferably with the use of a centrifuge.
11. A process according to any preceding claim in which the suspension is selected from the group consisting of sewage sludges, pulp and paper mill sludges, textile industry effluents, deinking sludges and food and animal process sludges.
12. An aqueous composition comprising 2 to 20 parts by weight of water-soluble cationic polymeric flocculant and one part by weight water-soluble anionic polymeric flocculant and sufficient water to give a polymer concentration of below 5% in which the anionic and cationic polymeric flocculants form stably suspended particles of counterionic precipitate of size at least 90 wt.% above 100 μm and substantially all the cationic polymer which is not part of the counterionic precipitate is in solution.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/00991

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C02F11/14 C02F1/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C02F C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 720 346 A (FLESHER PETER ET AL) 19 January 1988 (1988-01-19) claims 1-18; example 9 ---	1,4-6, 8-12
A	WO 97 06111 A (ALLIED COLLOIDS LTD ;ALLEN ANTHONY PETER (GB); MCCOLL PHILIP (GB);) 20 February 1997 (1997-02-20) cited in the application the whole document ---	1,3-12
A	US 5 112 500 A (JONES GRAHAM) 12 May 1992 (1992-05-12) claims 1-4 ---	1,4-6,8, 10-12
A	US 4 746 690 A (BUSCH PETER ET AL) 24 May 1988 (1988-05-24) claims 1-5 ---	1,4,5,12
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

15 July 1999

Date of mailing of the international search report

04/08/1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Gruber, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00991

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 673 704 A (FLESHER PETER ET AL) 16 June 1987 (1987-06-16) claims 1,2 ---	1,4-7,9, 11,12
A	US 4 104 226 A (MELZER JAROSLAV ET AL) 1 August 1978 (1978-08-01) claims 1-6 ---	1,4,5,8, 11,12
A	US 5 171 781 A (FLESHER PETER ET AL) 15 December 1992 (1992-12-15) claims 1-12 ---	1,4-9, 11,12
A	US 3 539 510 A (PRIESING CHARLES P ET AL) 10 November 1970 (1970-11-10) claims 1-10 ---	1,4,5,7, 8,11,12
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 126 (C-228), 13 June 1984 (1984-06-13) & JP 59 039398 A (UNITIKA KK), 3 March 1984 (1984-03-03) abstract ---	1,4,5,12
A	US 5 681 475 A (LAMENSDORF MARC ET AL) 28 October 1997 (1997-10-28) column 5, line 1-8; claims 1,9-11 -----	1,4,5,7, 8,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/00991

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4720346 A	19-01-1988	AU 5658386 A	06-11-1986
		AU 594671 B	15-03-1990
		AU 5658486 A	06-11-1986
		AU 581980 B	09-03-1989
		AU 5658586 A	06-11-1986
		CA 1277449 A	04-12-1990
		CA 1284933 A	18-06-1991
		CA 1277785 A	11-12-1990
		DK 188886 A,B,	26-10-1986
		DK 188986 A	26-10-1986
		DK 189086 A,B,	26-10-1986
		EP 0207592 A	07-01-1987
		EP 0201237 A	12-11-1986
		EP 0202780 A	26-11-1986
		FI 861722 A	26-10-1986
		FI 861723 A,B,	26-10-1986
		FI 861724 A	26-10-1986
		JP 2087416 C	02-09-1996
		JP 8000163 B	10-01-1996
		JP 61293509 A	24-12-1986
		JP 1986445 C	08-11-1995
		JP 7018871 B	06-03-1995
		JP 61275653 A	05-12-1986
		JP 8000164 B	10-01-1996
		JP 61293510 A	24-12-1986
		US 4943378 A	24-07-1990
		US 4820645 A	11-04-1989
		US 4759856 A	26-07-1988
WO 9706111 A	20-02-1997	AU 691124 B	07-05-1998
		AU 6665496 A	05-03-1997
		AU 703657 B	01-04-1999
		AU 7878898 A	01-10-1998
		CA 2223855 A	20-02-1997
		EP 0861214 A	02-09-1998
		PL 324895 A	22-06-1998
US 5112500 A	12-05-1992	AU 654137 B	27-10-1994
		AU 8064791 A	23-01-1992
		CA 2075946 A	30-12-1991
		EP 0536195 A	14-04-1993
		FI 925861 A	23-12-1992
		WO 9200248 A	09-01-1992
US 4746690 A	24-05-1988	DE 3518673 A	27-11-1986
		CA 1285681 A	02-07-1991
		EP 0209661 A	28-01-1987
		JP 61271356 A	01-12-1986
US 4673704 A	16-06-1987	CA 1238132 A	14-06-1988
		EP 0170394 A	05-02-1986
		JP 1918766 C	07-04-1995
		JP 6043498 B	08-06-1994
		JP 61034026 A	18-02-1986
US 4104226 A	01-08-1978	DE 2538281 A	10-03-1977
		AU 503560 B	06-09-1979
		AU 1604276 A	26-01-1978

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/00991

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4104226 A		CA 1050680 A	13-03-1979
		FI 762459 A	01-03-1977
		FR 2322197 A	25-03-1977
		GB 1549874 A	08-08-1979
		JP 52028546 A	03-03-1977
		NL 7609582 A	02-03-1977
		SE 410793 B	05-11-1979
		SE 7609474 A	01-03-1977
US 5171781 A	15-12-1992	GB 2200440 A,B	03-08-1988
		AU 612619 B	18-07-1991
		AU 1114488 A	04-08-1988
		AU 596055 B	12-04-1990
		AU 1114588 A	04-08-1988
		CA 1293351 A	24-12-1991
		DE 3869631 A	07-05-1992
		EP 0277017 A	03-08-1988
		EP 0277018 A	03-08-1988
		GB 2200133 A,B	27-07-1988
		US 4880858 A	14-11-1989
		US 5384343 A	24-01-1995
		AU 652053 B	11-08-1994
		AU 1705992 A	16-07-1992
		AU 2891589 A	03-08-1989
		CA 1339850 A	05-05-1998
		DE 68927982 D	28-05-1997
		DE 68927982 T	07-08-1997
		EP 0326382 A	02-08-1989
		JP 1315426 A	20-12-1989
US 3539510 A	10-11-1970	BE 716430 A	12-12-1968
		DE 1767749 A	29-04-1971
		FR 1580955 A	12-09-1969
		GB 1184003 A	11-03-1970
		JP 49033742 B	09-09-1974
		NL 6807859 A	13-12-1968
JP 59039398 A	03-03-1984	NONE	
US 5681475 A	28-10-1997	AU 5850596 A	30-10-1996
		CA 2218048 A	17-10-1996
		EP 0830205 A	25-03-1998
		WO 9632194 A	17-10-1996